

An Alkaline Solution of Potassium Chromate as a Transmittancy Standard in the Ultraviolet

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The need for a means of testing the reliability of the photometric scale of spectrophotometers in the ultraviolet region (where glasses are unsuitable) has led to the study of an aqueous solution of potassium chromate having the composition 0.0400 g/liter of K_2CrO_4 in 0.05 *N* KOH. Based on extensive measurements, using photographic, photoelectric, and visual spectrophotometry, standard values of spectral transmittancy have been determined for 1.000 and 2.000 cm of solution at 25° C from 220 to 500 $m\mu$. These values have been tabulated along with derived values of absorbancy, molar absorbancy index a_M , and $\log_{10} a_M$. The latter values have been compared graphically with those of other observers. Changes in spectral transmittancy with changes in temperature have been determined. The work has also included a study of the effects due to the container bottle and to age of solutions over periods up to 8 years, and a comparison of results obtained with the solution prepared either from K_2CrO_4 or from $K_2Cr_2O_7$ as one of the reagents.

1. Introduction

A means of testing the reliability of the photometric scale of spectrophotometers in the ultraviolet region has been in demand for a number of years. With the introduction of commercial photoelectric spectrophotometers for the ultraviolet in 1940, the demand increased considerably.

Although glass filter standards of spectral transmittance [1, 2]¹ have proved to be a very satisfactory and valuable means of testing the reliability of the photometric scale of spectrophotometers in the visible region, they are in general unsatisfactory in the ultraviolet. Not only do all but a few special glasses absorb completely below 290 $m\mu$, but, in addition, the ultraviolet spectral transmittances of many glasses change on exposure to strong ultraviolet radiant flux [2, 3, 4]. In these respects solutions in cells with quartz end plates are found to be superior to glasses for use in the ultraviolet. In addition, solutions are reproducible and can be prepared in the laboratory from specifications with relatively small time and cost. Various solutions have been studied or recommended^{2,3} for this purpose. Preeminent among these is an aqueous solution of potassium chromate, K_2CrO_4 (0.04 g/liter) in 0.05 *N* KOH. This has alternate regions of high transmission and absorption in the ultraviolet, and this one solution in 1- and 2-cm thicknesses covers the transmittancy scale from about 0.90 to about 0.01 (0.046 to 2.0 in absorbancy). Several investigators have previously worked with this solution, and from the information available in 1940 this appeared to be one of the best for the purpose. It was accordingly selected for calibration.⁴

To make the solution most useful as a calibration standard of spectral transmittancy in the ultraviolet, information should be available regarding its permanence, or stability, under specified conditions (including the effects of the container bottles on the spectral transmittancy) and regarding any change in its spectral transmittancy with temperature over the range of room temperatures to be expected. Such data have accordingly been obtained.

This investigation was started in 1940 and discontinued in 1943 because of the war. It was resumed in 1948, and preliminary data have been published [8, 9, 10]. The present paper describes the work leading up to the determination of these preliminary values, based solely on the measurements made in 1940-43, and describes the recent work on new solutions with a new instrument, on the basis of which the final values were derived as herein published.

2. Preparation of Solutions

All the potassium chromate solutions studied were prepared in the Bureau's Chemistry Division by W. Stanley Clabaugh. The solutions are of two general types (A) those prepared by dissolving the salt in dilute solution of KOH, and (B) those prepared by dissolving the salt in distilled water.

The type (A), or alkaline, solutions were prepared as follows:

(A₁): A solution of K_2CrO_4 stock material, reagent grade, 0.0400 g/liter, in 0.05 *N* KOH (solution of potassium hydroxide prepared by dissolving 3.3 g of potassium hydroxide sticks (85% KOH) of reagent

These solutions have their limitations for use as calibration standards both in the shortwave end of the visible region and in the ultraviolet region. In the visible, neither of them has sufficient absorption in the violet to be of much value for the purpose. In the ultraviolet, the copper sulfate solution varies rather rapidly from high transparency at wavelengths above 330 $m\mu$ to high absorption at wavelengths below 270 $m\mu$ and thus has no general utility over the whole region. The cobalt ammonium sulfate solution used in the Davis-Gibson filters [7] has too high transparency between 230 and 400 $m\mu$ to be of much value as a spectrophotometric standard. Solutions prepared at 10 times this concentration were found (unpublished data) to be unstable with time throughout the ultraviolet and were thus considered undesirable for use as spectrophotometric calibration standards.

¹ Figures in brackets indicate the literature references at the end of this paper.
² For example, Brode [5, p. 200] lists potassium chromate, azobenzene, and potassium nitrate as solutions that can be accurately prepared as standards for the calibration of spectrophotometers.

³ Photoelectric Spectrophotometry Group of England has recently conducted a collaborative test on the use of $K_2Cr_2O_7$ [6].

⁴ Solutions can, of course, also be used in the visible region. In fact, the aqueous solutions of copper sulfate and cobalt ammonium sulfate used in the Davis-Gibson filters [7, 8, 9, 10] have been recommended for that purpose.

quality in sufficient distilled water to make 1 liter).

(A₂): A solution of K₂CrO₄ of the same concentration and alkalinity as (A₁) but prepared from 0.0303 g of K₂Cr₂O₇⁵, which, when converted gave 0.0400 g of K₂CrO₄/liter. This follows from the reaction $K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O$.

The purpose of dissolving the potassium chromate in dilute solutions of KOH was to prevent any dichromate from forming. In A₂ a potassium chromate solution was prepared by means of a different material, potassium dichromate. This solution was prepared to determine whether the spectrophotometric data from A₁ and A₂ would be identical. Since they were found to be identical, there is a distinct advantage in using potassium dichromate as one of the reagents rather than potassium chromate, because in stock material potassium dichromate exists in a purer state. A special sample of potassium chromate that had been recrystallized four times was used in the preparation of one of the B, or neutral, solutions with the view to studying the effect of the purity of the potassium chromate.

The solutions prepared in 1940, 1942, and again in 1949 were stored in liter bottles of the ordinary storeroom glass type with glass stoppers. For further study of the effect of storage, half of the 1940 alkaline solution prepared from K₂CrO₄ and half of the 1940 neutral solutions were stored in similar bottles lined with ceresin. The tips of the rubber stoppers used were also covered with ceresin. Also half of the alkaline solutions prepared by methods A₁ and A₂ in 1949 were stored in alkali-resistant glass (Corning glass 728).

None of the solutions was exposed to light except when actually in use to fill the cells for their measurement. No solution was ever poured out of its bottle. In filling the cells a pipette was used to draw off the solution. Where flaking occurred, the sediment thus remained on the bottom of the bottle. Each cell containing solution was measured relative to a similar cell containing distilled water.

The alkaline solutions are those from which the standard set of spectral transmittancies given in table 1 were obtained. Although both alkaline and neutral solutions were prepared originally for the purpose of establishing standard spectral transmittancy data, the neutral solutions were finally not used for that purpose. However, as the neutral solutions have been studied over a period of 8 years, a summary of the results on these is included in section 8.

3. Methods of Measurement

The solutions were measured on five instruments by three different methods. One instrument operates by a photographic method, primarily for the ultraviolet region, but extending also into the violet and blue; one by a visual method; and three by photoelectric, one of these being for the visible range only.

⁵ Standard Sample K₂Cr₂O₇, No. 136, may now be obtained from the National Bureau of Standards. At the time these solutions were prepared, the chemicals used all conformed to ACS specification.

3.1. Photographic Method

The photographic data were obtained by means of the Hilger sector photometer with the Fuess quartz spectrograph [11, 12, 13].

The equivalent slit widths for an 0.2-mm slit, which was used throughout all the exposures, are

Wavelength	Slit widths	
<i>mμ</i>	<i>mm</i>	<i>mμ</i>
400	0. 2	0. 6
310	. 2	. 25
260	. 2	. 13
220	. 2	. 08

On each plate exposures were made of at least two aluminum spark spectra for wavelength calibration purposes. A calibration curve was used to translate scalar values, which were read at the density match-points, into wavelengths. Both 1.000- and 4.000-cm cells were used with the Hilger instrument.

3.2. Visual Method

The König-Martens spectrophotometer [13, 14] is a visual instrument. The slit widths used on this instrument are varied, depending upon the wavelength and the spectral characteristics of the sample being measured. With an incandescent source the equivalent slit widths in millimicrons used for two wavelengths and for two settings of the slits are given below:

Wavelength	Slit widths	
<i>mμ</i>	<i>mm</i>	<i>mμ</i>
400	0. 5	2. 7
500	. 2	2. 7

The mercury arc, also available for use on this instrument, enables transmittancy measurements to be made that are not subject to possible wavelength or slit-width errors.

Two cell lengths were used with this instrument, namely, 4.000 and 10.000 cm.

3.3. Photoelectric Method

a. Brackett Quartz Double Monochromator and Auxiliary Equipment [15]

The source of illumination used was a special incandescent lamp, with a quartz window, which operated on a 120-volt, 45-ampere battery. The monochromator has three slit systems. The exit slit next to the photoelectric tube was kept at a constant mechanical width for nearly all the measurements, and the other two were varied concurrently. Any stray energy that passes the second slit is effectively eliminated from reaching the exit slit by the use of the second spectrometer provided on this instrument.

The instrument operates with a single wavelength control. Spectral bands transmitted by the slits were comparable in width ($m\mu$) to those obtained with the photographic method. A photoelectric cell of the electron-emission type was used as detector and values of spectral transmittancy were obtained by means of the ratio-of-deflections method with a high-sensitivity galvanometer.

The scale for reading or setting wavelengths on this monochromator is a linear one (not direct reading in millimicrons) and a wavelength calibration curve of the instrument was already available.⁶ This curve was based upon scalar settings previously determined for mercury lines down to 237.8 $m\mu$. As the incandescent lamp was the only source of irradiation for the spectrophotometric work, the wavelength calibration was frequently checked at one wavelength (557 $m\mu$) by means of two particular standard glasses whose spectral transmittances are known to be the same at that wavelength. The linear correction determined at this wavelength was then applied to the whole scale.

The lower end of the wavelength calibration curve was extrapolated below 237.8 $m\mu$ for these measurements, and the data in this region with the Brackett instrument are therefore of lesser validity.

b. General Electric Recording Spectrophotometer

The General Electric recording spectrophotometer has been described in a series of three papers [16, 17, 18]. The data obtained with this instrument are for the visible range only and extend from 400 to 750 $m\mu$. Checks on the wavelength scale were made in the usual manner by using a calibrated didymium glass. A nominal slit width equivalent to approximately 4 $m\mu$ was used throughout the recordings. Cells of 1.000-cm thickness were used for the measurements.

c. Beckman Quartz Spectrophotometer (Model DU)

The Beckman spectrophotometer has been described in a paper by Cary and Beckman [19]. Transmission measurements with a modification of this instrument, which has a constant-temperature enclosure⁷ designed and constructed at the National Bureau of Standards, have been described in detail in a paper by Gibson and Balcom [20]. All measurements on the Beckman spectrophotometer were made with a 1.000-cm cell. The cell holder is kept constant at 25° C or other desired temperature by means of water pumped through from a constant-temperature bath.

For wavelength checks the Hg green line (546.1 $m\mu$) was used. When necessary, the whole wavelength scale was adjusted by the slight turning of

the internal screw that rotated the collimating mirror. After such check or adjustment, the precise wavelength correction was then applied at each wavelength setting in accordance with the curve illustrated in figure 6 of reference [20].

For transmittancy measurements three sources are available, namely, the incandescent-filament lamp, the hydrogen arc, and the mercury arc, all as supplied by the maker. The incandescent and hydrogen sources were used over the appropriate wavelength ranges, overlapping from 320 to 380 $m\mu$. The slit widths with these sources never exceeded 2 $m\mu$ and were usually less than 1 $m\mu$. The mercury arc was also used for transmittancy measurements at certain wavelengths as noted below.

A clear quartz lens similar to that supplied with the instrument was used to effect an approximate collimation of the beam. Over the wavelength range from 330 to 420 $m\mu$ with the incandescent source and from 360 to 380 $m\mu$ with the hydrogen source, a purple (Corning filter No. 9863) lens was used to reduce stray light as well as to collimate the beam.

4. Standard Spectrophotometric Data

In examining the data obtained during the first two years of the investigation, the type A, or alkaline, solutions were found to give more reproducible results (i. e., less scattering of data on repeated measurements) than the type B, or neutral, solutions. Furthermore, the alkaline solutions were found to give a better range of transmittancies in the extreme ultraviolet than the neutral solutions. Since the alkaline solutions were thus found to fulfill more nearly the requirements of a standard of spectral transmittancy in the ultraviolet, all later work and all the detailed data to be presented refer to the alkaline solution of potassium chromate (0.04 g/liter in 0.05 N KOH).

As already noted, the work on the 1940 and 1942 solutions was interrupted in 1943. Sufficient data were obtained, however, that a tentative set of spectral transmittancy values could be evaluated. These values are given⁸ in column 2 of table 1, designated as T'' . They were read from a curve, of which figure 1 is a tracing. The individual determinations by the five instruments used are plotted and may be identified from the legend. These tentative values thus represent a graphical average of all these earlier data. Measurements were made on the 1940 solutions a few days after their preparation and then again at the end of 2, 4, 7, 8, and 10 months, 2 years 4 months, 2 years 5 months, and 2 years 7 months. The 1942 solutions were measured a few days after their preparation and again in 1, 2, and 6 months.

⁶ Acknowledgment is here made to W. F. Roeser and M. S. Van Dusen for making the instrument and its calibration curve available.

⁷ In 1942 a few measurements on a Beckman quartz spectrophotometer in the Bureau's Chemistry Division were made on an alkaline solution prepared in 1940. No temperature control was available for these measurements.

⁸ These tentative values have also been published in [8; 9, p. 43-44; 10, p. 261].

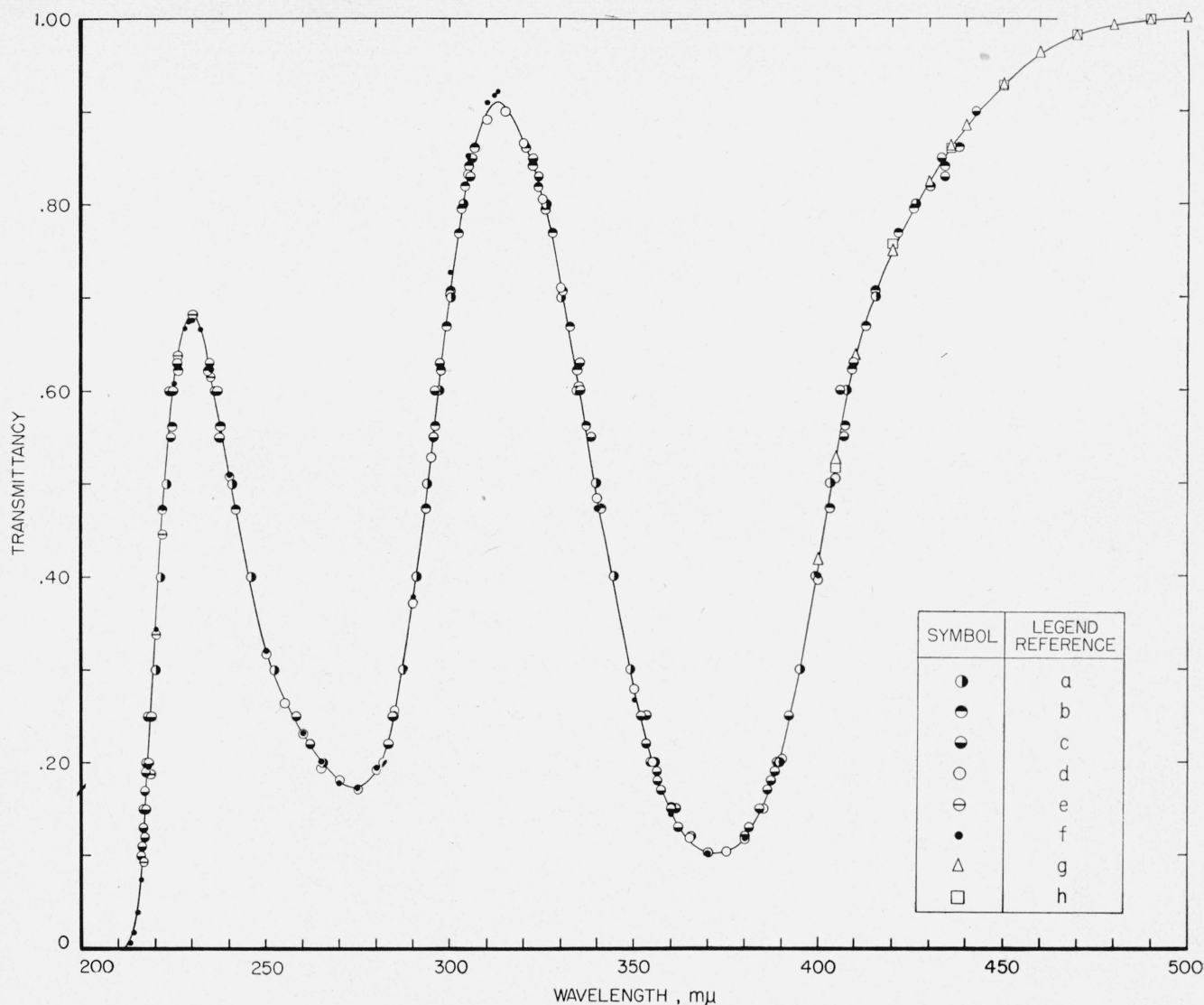


FIGURE 1. Tracing of original curve from which tentative values of spectral transmittancy, T'_s , were read (table 1, column 2) and published [8, 9, 10] for potassium chromate solution (0.0400 g/liter of K_2CrO_4 in 0.05 N KOH)

Distilled water only was used in the solvent cell. These data were obtained in 1940 and 1942, as follows:

	Spectrophotometer	Wavelength range used	Alkaline solution prepared	Cell length	Number of determinations represented
a	Hilger sector photometer (photographic).	215 to 450....	A ₁ , 1940..	1	5 to 7
b			A ₂ , 1940..	1	
c			A ₁ , 1940..	4	1
d	Brackett double monochromator (photoelectric).	240 to 404.7..	A ₁ , 1940..	1	1 to 3
e			A ₁ , 1940..	1	
f			A ₂ , 1940..	1	2 to 5
g	GE automatic recording (photoelectric).	Adjusted below 240.	A ₁ , 1942..	1	2
h			A ₂ , 1942..	1	
			A ₁ , 1940..	1	1
	König-Martens (visual).	400 to 750....	A ₁ , 1942..	1	4
			A ₂ , 1942..	1	
			A ₁ , 1940..	4	1 to 4
			A ₂ , 1940..	10	

TABLE 1. Spectrophotometric data for a standard potassium chromate solution (0.0400 g/liter in 0.05 N KOH), unfiltered, at 25° C

The final values of spectral transmittancy, T_s , and absorbancy, A_s , for 1.000 cm determined from this investigation are shown in columns 5 and 9. Derived from these data are values of T_s for 2.000 cm, molar absorptivity index, a_M , and $\log_{10} a_M$, columns 10, 11, and 12. The tentative values of transmittancy, T'_s , which have been published [8, 9, 10] were taken from column 2. The solution was measured in every case relative to a similar cell containing distilled water.

Wave-length	Transmittancy, T_s , for 1.000 cm							Absorbancy, $A_s = -\log_{10} T_s$ for 1 cm	Transmittancy, T_s , for 2 cm	Molar absorptancy index, a_M ($a_M = A_s/bc$) ^b	$\log_{10} a_M$
	Tentative values of T'_s ^a based on 1940-42 data (read from fig. 1)	Beckman 1949 data, 25° C		Final values of T_s (5/24/49)	Deviations from final values						
		Hg source	H and/or incandescent sources		1940-42 data (2) - (5)	1949 Beckman					
						Hg values (3) - (5)	H, and/or incandescent values (4) - (5)				
1	2	3	4	5	6	7	8	9	10	11	12
$m\mu$											
210	0.000										
15	.037		0.070								
20	.35		.358	0.358	-0.008		0.000	0.446	0.128	2167	3.34
25	.60		.601	.601	-.001		.000	.221	.361	1074	3.03
30	.682		.667	.674	+0.008		-.007	.171	.454	832	2.92
35	.617		.615	.616	+0.001		-.001	.210	.379	1022	3.01
40	.509		.505	.507	+0.002		-.002	.295	.257	1433	3.16
45	.408		.397	.402	+0.006		-.005	.396	.162	1922	3.28
50	.319		.319	.319	.000		.000	.496	.102	2410	3.38
53.6	.279	0.278	.280	.279	.000	-0.001	+0.001	.554	.078	2693	3.43
55	.268		.268	.268	.000		.000	.572	.072	2778	3.44
60	.232		.234	.233	-.001		+0.001	.633	.054	3072	3.49
65	.201		.204	.202	-.001		+0.002	.695	.041	3374	3.53
70	.180		.181	.180	.000		+0.001	.745	.032	3617	3.56
75	.173		.178	.175	-.002		+0.003	.757	.031	3676	3.57
80	.189		.199	.194	-.005		+0.005	.712	.038	3459	3.54
85	.254		.261	.257	-.003		+0.004	.590	.066	2866	3.46
90	.372		.374	.373	-.001		+0.001	.428	.139	2080	3.32
95	.527		.536	.533	-.006		+0.003	.273	.284	1327	3.12
96.7	.590	.605	.600	.598	-.008	+0.007	+0.002	.223	.358	1084	3.04
300	.703		.710	.709	-.006		+0.001	.149	.503	726	2.86
02.2	.764	.779	.770	.771	-.007	+0.008	-.001	.113	.594	548	2.74
05	.831		.834	.834	-.003		.000	.079	.696	383	2.58
10	.899		.888	.895	+0.004		-.007	.048	.801	234	2.37
13.2	.910	.907	.897	.905	+0.005	+0.002	-.008	.043	.819	211	2.32
15	.904		.893	.900	+0.004		-.007	.046	.810	222	2.35
20	.867		.860	.864	+0.003		-.004	.064	.746	308	2.49
25	.810		.797	.804	+0.006		-.007	.095	.646	460	2.66
30	.715		.706	.710	+0.005		-.004	.149	.504	722	2.86
34.2	.622	.620	.619	.620	+0.002	.000	-.001	.208	.384	1008	3.00
35	.603		.598	.600	+0.003		-.002	.222	.360	1077	3.03
40	.486		.480	.483	+0.003		-.003	.316	.233	1535	3.19
45	.379		.367	.373	+0.006		-.006	.428	.139	2080	3.32
50	.281		.272	.276	+0.005		-.004	.559	.076	2715	3.43
55	.202		.196	.199	+0.003		-.003	.701	.040	3405	3.53
60	.148		.148	.148	.000		.000	.830	.022	4030	3.61
65	.115	.114	.118	.116	-.001	-.002	+0.002	.936	.013	4544	3.66
70	.102		.104	.103	-.001		+0.001	.987	.011	4795	3.68
75	.103		.102	.102	+0.001		.000	.991	.010	4815	3.68
80	.118		.116	.117	+0.001		-.001	.932	.014	4526	3.66
85	.152		.147	.150	+0.002		-.003	.824	.022	4002	3.60
90	.207		.198	.202	+0.005		-.004	.695	.041	3374	3.53
95	.301		.287	.294	+0.007		-.007	.532	.086	2582	3.41
400	.410		.395	.402	+0.008		-.007	.396	.162	1922	3.28
04.7	.521	.515	.508	.515	+0.006	.000	-.007	.288	.265	1400	3.15
10	.635		.630	.632	+0.003		-.002	.199	.399	968	2.99
20	.748		.754	.751	-.003		+0.003	.124	.564	604	2.78
30	.824		.824	.824	.000		.000	.084	.679	408	2.61
35.8	.861	.860	.856	.859	+0.002	+0.001	-.003	.066	.738	320	2.51
40	.884		.880	.882	+0.002		-.002	.054	.778	265	2.42
50	.928		.926	.927	+0.001		-.001	.033	.859	160	2.20
60	.961		.959	.960	+0.001		-.001	.018	.922	86	1.93
70	.981		.979	.980	+0.001		-.001	.009	.960	43	1.63
80	.992		.990	.991	+0.001		-.001	.004	.982	19	1.28
90	.998		.996	.997	+0.001		-.001	.001	.994	6	.80
500	1.000		.999	1.000	.000		-.001	.000	1.000		

^a These values were read from the original of figure 1 and are consistent with the values published later [8, 9, 10].^b $c = 0.0002059$ M; $b = 1$ cm.

In April 1949 four sets of data were taken on the Beckman spectrophotometer [20], one on each of freshly prepared alkaline (A_1 and A_2) solutions maintained at 25° C, stored both in glass and alkali-resistant ware.

The four sets of data were averaged. Values obtained with the mercury source are listed in column 3 of table 1; values obtained with the hydrogen and/or incandescent sources are listed in column 4.

The final values of T_s shown in column 5 were derived according to the following procedures:

(a) At the mercury wavelengths, a straight average of three sets of data, namely, (1) 1949 Beckman data with mercury line source (column 3); (2) 1949 Beckman data with hydrogen and/or incandescent continuous-spectrum source (column 4); (3) Tentative values based on 1940–42 data, T'_s , (column 2).

(b) At other wavelengths above 220 $m\mu$ (with the exception of 295 to 315) a straight average of two sets of data, namely, (1) 1949 Beckman data with hydrogen and/or incandescent source (column 4); (2) Tentative values based on 1940–42 data, T'_s (column 2).

At 295, 300, 305, 310, and 315 $m\mu$ slight further adjustments in T_s (not exceeding 0.003) were made to bring the final values into better agreement with the averages obtained at the mercury wavelengths, using procedure (a).

Columns 6, 7, and 8 of table 1 show the deviations of the three sets of data from the final values. It is evident that there may be considerable uncertainty in the third decimal of column 5.

Values of spectral absorbancy, A_s , for a 1.000-cm thickness of solution are given in column 9. These values of A_s were derived from the relation $A_s = -\log_{10} T_s$. To cover the photometric scale below $T_s = 0.10$, values of transmittancy for a 2.000-cm cell were computed and are given in column 10.

Column 11 gives values of the molar-absorbancy index [21] $a_M \equiv A_s/bc$ where c is the concentration expressed in moles per liter, and b is the cell thickness in centimeters. Column 12 gives the values of $\log_{10} a_M$.

5. Comparison of Data with Those of Other Observers

Tabular data on the spectral transmittancy of potassium chromate in 0.05 *N* potassium hydroxide have been published by von Halban and Siedentopf [22], Rössler [23], Baly, Morton, and Riding [24], and Hogness, Zscheile, and Sidwell [25].

Hogness, Zscheile, and Sidwell used a photoelectric method for their determinations. The potassium chromate was recrystallized four and five times. They show the absorption spectrum for this solution in a figure [25]. The dots through which the curve is drawn in their figure are taken from several series of determinations at 2.5- $m\mu$ intervals from 220 to 410 $m\mu$. Values of molar extinction for the maxima and minima and for 366 and 265 $m\mu$ were given in tabular form. The experimental conditions under which these tabulated data were obtained are given in table 2.

Figure 2 compares the present data with those already published in tabular form. $\log_{10} a_M$ is used for this comparison in accord with the practice used in the International Critical Tables [26]. The methods used in the various studies are shown in the caption.

TABLE 2. *Experimental conditions under which certain data of Hogness, Zscheile, and Sidwell [25] were obtained*

Wavelength	Molar-absorbancy index	Spectral region isolated	Cell thickness	Concentration	
$m\mu$	a_M	$m\mu$	cm	g/liter	M
Maxima:					
272.5.....	3660	0.74	2	0.00860	0.04428×10^{-3}
371.0.....	4830	1.32	2	.00650	.03347
Minima:					
229.0.....	752	.72	2	.0400	.2059
312.5.....	203	1.10	7	.0400	.2059
Mercury lines:					
265.0.....	3460	-----	2	.00765	.0394
366.0.....	4720	-----	2	.00575	.0296

From figure 2 it may be seen that in general the agreement in $\log_{10} a_M$ from 220 to 450 $m\mu$ found by the five investigators shown is quite close, with the exception of a few points. Below 300 $m\mu$, two values of von Halban (photoelectric method) at 254 and 265 $m\mu$ are at variance with the rest. Above 300 $m\mu$, the value of Baly, Morton, and Riding (photographic method) at 313.2 $m\mu$, seems erroneous. Most of the 16 wavelength values of Rössler from 381.5 to 439.0 $m\mu$ will be seen to be lower in $\log_{10} a_M$ than those of the others shown. In his paper, Rössler has put these wavelengths in parentheses; apparently these were so indicated because of the relatively low dispersion of the prism in his instrument.

In the present investigation only a single concentration of potassium chromate was used. No attempt was made to carry out a study of conformity to Beer's law, because the one solution in 1- and 2-cm thicknesses covered the photometric range of interest. However, it was known that Hogness, Zscheile, and Sidwell had made a run on exactly the same concentration used by von Halban and found good agreement with their curve [25] obtained from data on optimum concentration. From these data it was concluded that Beer's law held. Results have also been published [27] of Beer's law tests on potassium chromate in 0.05 *N* KOH at 372 $m\mu$. Various dilutions were used, and the results are given in both tabular and graphical forms. The molecular concentrations used varied from 1.61×10^{-5} to 51.5×10^{-5} . This corresponds to variations in concentration from 0.00313 to 0.1000 g/liter. Determination of this compliance with Beer's law was made as a means of checking the photometric reproducibility of a new spectrophotometer.

6. Effect of Temperature on Spectral Transmittancy

Because it was desirable to know whether or not the potassium chromate solution for use as a calibration standard changed in spectral transmittancy

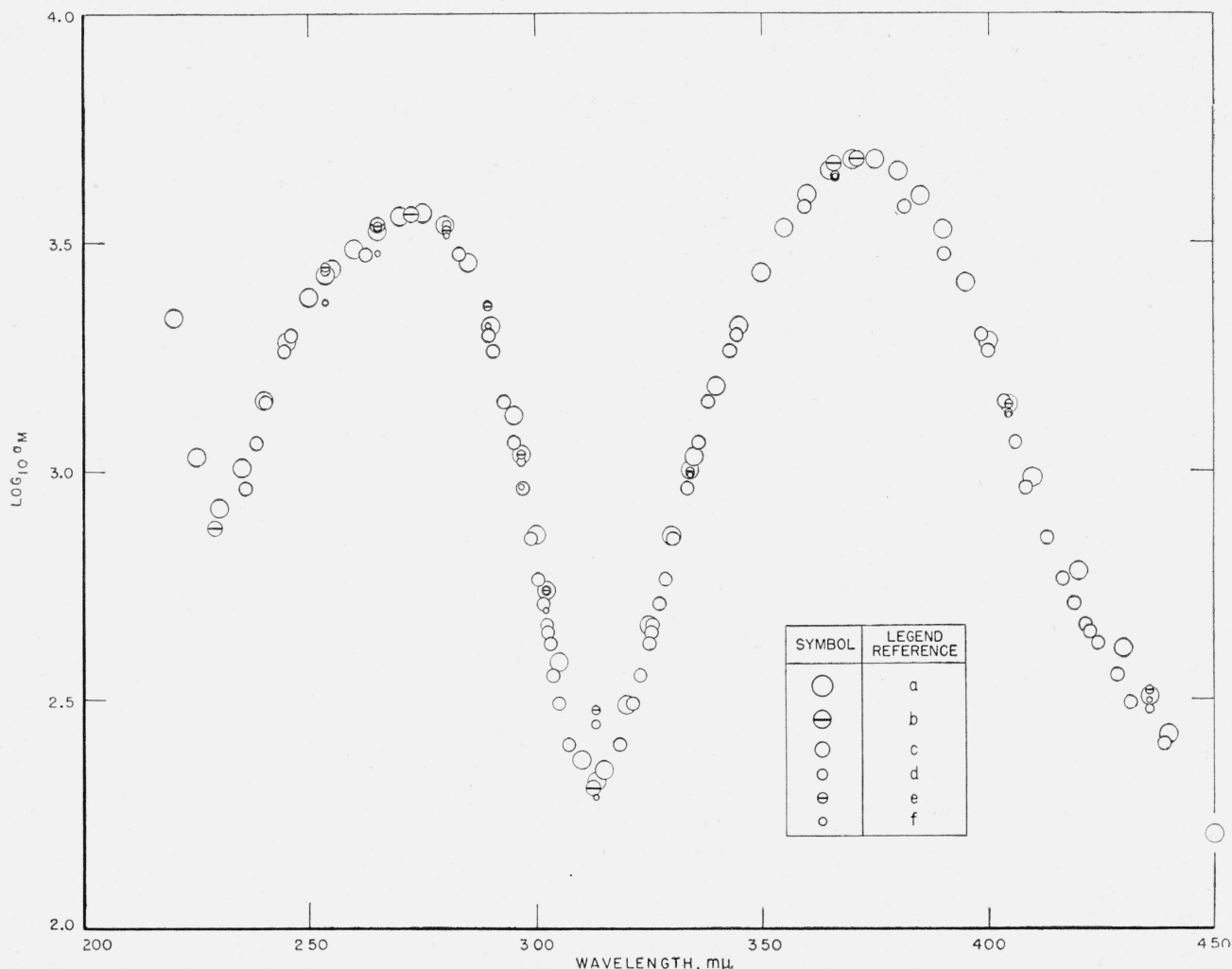


FIGURE 2. Values of $\log_{10} a_M$ for potassium chromate.

Molar solution in 0.05 N KOH. $b=1$ cm; $a_M = A_s/bc = -\log_{10} T_s/bc$.
 a. From NBS final data, column 12 of table 1.
 b. Hogness, Zscheile, Sidwell; photoelectric.
 c. Rössler; photographic.
 d. Baly, Morton, and Riding-Hilger rotating sector; photographic.
 e. Baly, Morton, and Riding Judd-Lewis sector; photographic.
 f. von Halban; photoelectric.

with change in temperature, several preliminary tests were made in 1948 on the 1942 solutions by means of the Beckman spectrophotometer [20]. The resulting data indicated that the largest effects due to changes in temperature occur below 235 $m\mu$.

A more detailed and complete study of the change in spectral transmittancy with temperature was then made for the 1949 alkaline solutions of both types stored in alkali-resistant bottles. The wavelength range from 215 to 500 $m\mu$ was studied for approximately a 25-deg change in temperature. The spectral-transmittancy data were determined for one solution over a definite wavelength range at 25°, 50°, and again at 25° C in a single day. Each change in spectral transmittancy for an approximately 25-deg change in temperature was computed separately for each day's set of measurements. Three sets

were averaged and are plotted in large circles in figure 3.

Included in the figure are also points obtained from the measurements made on the 1942 alkaline solutions at various times at each of the temperatures, 25° and 50° C. These data corroborate the data obtained with the 1949 solutions. It may be of interest to point out that the changes in transmittancy with increase in temperature shown in figure 3 are such as to indicate a shift of the absorption bands toward longer wavelengths.

The curve shown in figure 3 was then drawn, from which values of ΔT_s for a change of 25 deg were read. Values of ΔT_s for a change of 10 deg were computed from these curve readings by linear interpolation, and the resulting data are given in table 3. Users of the standard solution should

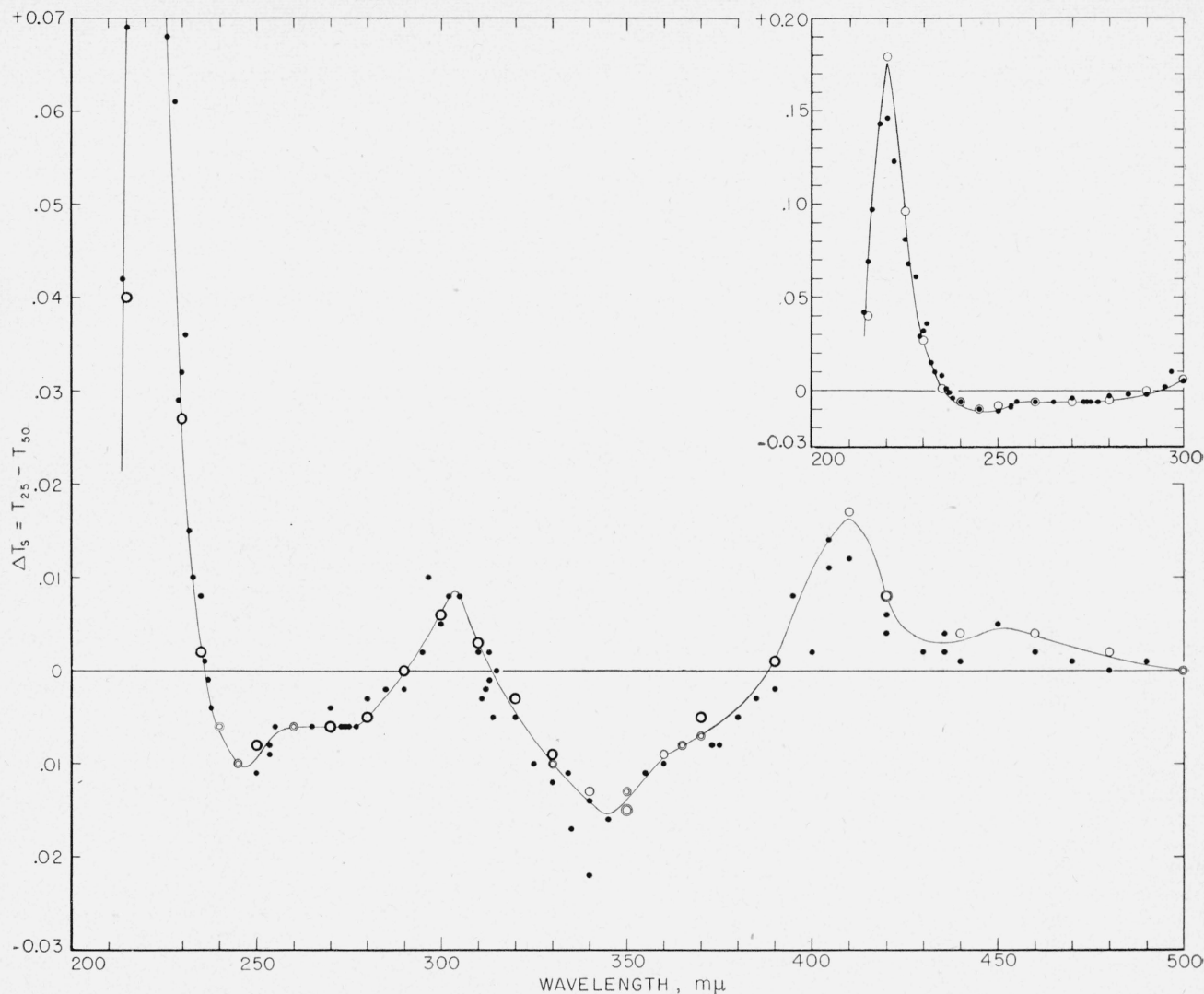


FIGURE 3. Change in spectral transmittancy for a change in temperature of 25° C.

In establishing this curve more weight has been given to the data obtained from the 1949 solutions. The values of ΔT_s given in table 3 for a 10° change in temperature were derived from this curve by linear interpolation.

○, $\Delta T_s (= T_{25} - T_{50})$ for 1949 solutions. (The measurements were all made on the same day.)
 ●, ΔT_s for 1942 solutions. (The measurements were made in 1948, mostly on different days.)

make use of these corrections proportionately whenever the temperature of the solution deviates importantly from 25° C. Values of ΔA_s in table 3 are derived from the values of ΔT_s by the relation.

$$\Delta A_s = -\log_{10} e \frac{\Delta T_s}{T_{s(\text{avg})}}.$$

7. Permanence

Measurements have been made from time to time on these alkaline solutions, and the study has included effects due to the storage of some of the solutions over periods up to 8 years. The 1940 alkaline solution made from K_2CrO_4 in KOH was stored both in an ordinary glass bottle and in a

similar bottle lined with ceresin. The 1940 alkaline solution made from $\text{K}_2\text{Cr}_2\text{O}_7$ and the 1942 alkaline solutions made both from chromate and dichromate were stored only in ordinary glass bottles.

Above 260 $\text{m}\mu$ no definite change in spectral transmittancy was found for the solutions stored in glass. Below 260 $\text{m}\mu$ the 1940 alkaline solutions showed definite changes at the end of 8 years of storage in glass bottles, the solution made from the dichromate exhibiting the smaller change. The fact that potassium dichromate in stock material exists in a purer state may account for this solution being more stable. However, the 1942 alkaline solutions of both types likewise stored in glass bottles showed little if any change in spectral transmittancy over a period of 6 years.

TABLE 3. Values of ΔT_s ($=T_{25}-T_{35}$ or $T_{15}-T_{25}$) for a 10°C change in temperature corresponding to wavelengths listed

These values are for a cell length of 1.000 cm and are two-fifths of the values read from the curve of figure 3. Values of ΔA_s are derived from the values of ΔT_s .

Wave-length	Values of ΔT_s for 10 deg. C	Values of ΔA_s for 10 deg. C	Wave-length	Values of ΔT_s for 10 deg. C	Values of ΔA_s for 10 deg. C
$m\mu$			$m\mu$		
210	-----	-----	330	.0040	.0024
15	+0.028	-0.22	34.2	.0047	.0033
20	.070	.094	35	.0049	.0035
25	.035	.026	40	.0056	.0050
30	.0100	.0065	45	.0062	.0072
35	+.0010	-.0007	50	.0056	.0087
40	-.0026	+.0022	55	.0046	.0099
45	.0040	.0043	60	.0037	.0107
50	.0038	.0051	65	.0033	.0122
53.6	.0030	.0046	70	.0028	.0116
55	.0027	.0044	75	.0022	.0093
60	.0024	.0045	80	.0016	.0059
65	.0024	.0051	85	-.0007	+.0020
70	.0024	.0058	90	+.0005	-.0011
75	.0024	.0059	95	.0024	.0036
80	.0020	.0045	400	.0043	.0047
85	.0011	.0019	04.7	.0056	.0047
90	-.0001	+.0001	10	.0065	.0045
95	+.0011	-.0009	20	.0032	.0019
96.7	.0016	.0012	30	.0013	.0007
300	.0025	.0015	35.8	.0012	.0006
02.2	.0031	.0017	40	.0013	.0006
05	.0032	.0017	50	.0018	.0008
10	.0012	-.0006	60	.0015	.0007
13.2	+.0001	.0000	70	.0010	.0004
15	-.0004	+.0002	80	.0006	.0003
20	.0018	.0009	90	+.0002	-.0001
25	.0030	.0016	500	.0000	.0000

For the 1940 alkaline solution made from K_2CrO_4 in KOH and stored in a ceresin-lined bottle, measurements from time to time showed that changes in absorption were occurring. Data obtained at the end of an 8-year period showed that complete absorption had occurred below $370\text{ m}\mu$. Obviously, therefore, an ordinary glass bottle is better for storage of a solution of potassium chromate in KOH than a ceresin-lined bottle. No study of the permanence of the alkaline solutions stored in alkali-resistant bottles has been made.

It must also be concluded from this study that since the data below $260\text{ m}\mu$ show possibility of a change in spectral transmittancy after a 6-month period, solutions no older than 6 months should be used for the photometric calibration of a spectrophotometer in this region of the spectrum. On the other hand, for regions above $260\text{ m}\mu$, it seems safe to use alkaline solutions of either type stored in ordinary glass bottles up to a period of 5 years.

8. Neutral Aqueous Solutions of Potassium Chromate

Considerable data were obtained on the B solutions (see section 2) and a summary is presented here.

The spectral-transmittancy curve of neutral solutions of potassium chromate was found by Hantzsch [28] to differ somewhat from the alkaline solution, and the results reported here corroborate this finding. From 400 to $500\text{ m}\mu$ the curve for the neutral solution is less steep than that of the alkaline solution with a crossing point at about $440\text{ m}\mu$, above which the

transmittancy of the alkaline solution is slightly higher. Between 300 and $330\text{ m}\mu$ the neutral solution is slightly lower in transmittancy than the alkaline solution and slightly higher both below and above this range up to $440\text{ m}\mu$. Below $230\text{ m}\mu$ this difference is large, the transmittancy at $215\text{ m}\mu$ being 0.40 for the neutral solution and 0.07 for the alkaline. The value (0.07) for this wavelength may be found in table 1, column 4. More weight should be given the 1949 Beckman data below $225\text{ m}\mu$, because the measurements were obtained under closely controlled conditions of temperature and while the solutions were still fresh, two important controls for this particular region (sections 6 and 7). However, this particular value may be somewhat in error due to another cause, namely, the possible presence of impurities in the KOH.

Over a period of years the neutral solutions were found to be more permanent than the alkaline solutions. Significant changes from 8-year storage in a glass bottle were confined to the spectral region below $230\text{ m}\mu$; and for storage in a ceresin-lined bottle changes were found only below $260\text{ m}\mu$. A specially pure sample (recrystallized four times) changed still less. The neutral solutions did not cause flaking in the bottles as the alkaline solutions do.

From the standpoint of permanence and convenience in storage the neutral solutions are slightly superior to the alkaline solutions, and had they been found equally reproducible the neutral solutions might be preferable as spectral transmittancy standards instead of the alkaline solutions.

9. Summary

Spectrophotometric studies of neutral and alkaline aqueous solutions of potassium chromate extending over a period of years have shown that the alkaline solution is the better suited for use as a spectral-transmittancy standard in the ultraviolet. The spectral transmittancy of this solution has been determined by five spectrophotometers used according to three different methods, and the final values are given in table 1 from 220 to $500\text{ m}\mu$. The final results are also expressed there in terms of absorbancy, $A_s = -\log_{10} T_s$, for a 1-cm cell; molar absorbancy index, $a_M = A_s/bc$; and $\log_{10} a_M$. Changes of transmittancy with temperature were evaluated, and correction data for deviations from the standard temperature of 25°C are given in table 3.

When stored in ordinary glass bottles, the solution is reasonably stable for 5 or 6 years. For work of the highest precision, however, to avoid unsuspected errors from any cause, it is recommended that solutions not over 6 months old prepared from chemicals of the highest purity be used as transmittancy standards.

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